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(6) STUDIES OF THE GaAs/OXIDE INTERFACE USING A LIQUID ELECTRODE.

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   a. Electrochemical Measurements of Interface States at the GaAs/Oxide Interface, K. W. Frese, Jr., and S. R. Morrison, J. Electrochem. Soc. 126, 1235 (1979).

   b. Electrochemical Measurement of States on Oxidized GaAs, K. W. Frese, Jr., and S. R. Morrison, J. Vac. Sci. Tech. 17, 609 (1980).

   c. Passivation and Interface State Studies on n-GaAs, K. W. Frese, Jr., and S. R. Morrison, submitted to J. Electrochem. Soc. (1980).

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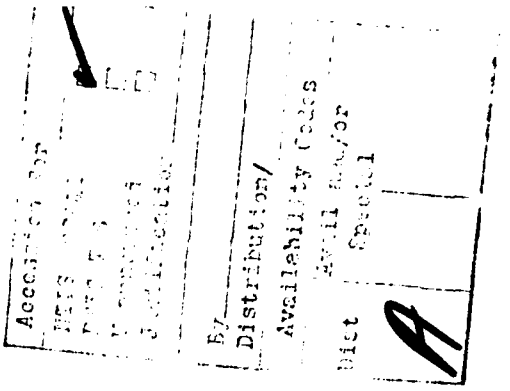
9. PAPERS GIVEN:

   a. Electrochemical Measurements of States on Oxidized GaAs, K. W. Frese, Jr., and S. R. Morrison, PCSI-6 Meeting, Asilomar, California, January 1979.

   b. The Conductance of the Native Insulating Oxide on GaAs, K. W. Frese, Jr., and S. R. Morrison, The Electrochemical Society Meeting, Los Angeles, California, October 1979.



TECHNICAL SUMMARY

Problem Studies

The objective of this study was twofold: first, to identify the material problems of the native oxide on GaAs that have prevented its successful use in MOSFET devices, and second, to attempt to overcome these problems and produce an electrically stable insulating film. This basic study was suggested because GaAs, with its high electron mobility, has potential value in high frequency integrated circuit applications (for computer and microwave applications). The difficulty in using GaAs for such applications is primarily associated with the difficulty of providing a good oxide. The oxide should have a high resistivity, and the density of oxide/semiconductor interface states should be low.

The study of the properties of the native oxide is simplified considerably by the use of electrochemical techniques. For example, using electrochemical techniques, we were able to make the capacity/voltage measurements that are normally used to describe the characteristics of MOS devices. However, as discussed in many reports and papers, we were able to overcome the difficulties encountered with the MOS method where a metal counterelectrode (instead of our liquid counterelectrode) permits high leakage currents and low breakdown fields. Measurements are available also with the electrochemical technique that cannot be duplicated by the MOS measurement. For example, very thin oxides in the earlier stages of anodic growth were amenable to study.

Summary of Important Results

It was determined that as normally grown, the native oxide on GaAs has an impurity band at about 1.0 eV below the GaAs conduction band. When the density of states in this band is very high, the n-GaAs/native oxide interface acts almost as a Schottky diode, with the oxide acting as the metal. Actually this band may well be the band that makes n-GaAs

MOS solar cells have such a high open circuit voltage.

It was concluded from calculation and experiment that this band is associated with excess elemental arsenic in the oxide. The gallium in the GaAs, being much more electropositive, will oxidize much more easily. Therefore we concluded that during the growth of the oxide (by the normal methods) there is so much more driving force for the gallium to oxidize that unoxidized arsenic is left buried as the GaAs/oxide interface moves along. It was also concluded that excess arsenic was left on the surface of the GaAs during acidic (particularly HCl) etching processes. After acidic etches, Auger spectroscopy measurements of a GaAs crystal showed excess arsenic on the surface. The longer the surface was exposed to an acid etch, the more excess arsenic was present. When the resulting surface was oxidized anodically (with varying degrees of difficulty), this excess arsenic appeared as interface states. The more the crystal was subjected to an acid etch, the poorer were the electrical properties of the subsequently grown oxide. We attribute the arsenic layer after an acid etch to the fact that elemental arsenic is quite noble and difficult to etch with the acid etches usually applied to GaAs.

Several methods were used to correct the difficulties, with some success. For example, the use of an oxidizing etch rather than an acid etch prevented most of the problems caused by the arsenic layer. With an oxidizing etch any excess arsenic was undetectable by Auger analysis, and the properties of the subsequent oxide were substantially improved. As another example of a method to avoid the arsenic, low currents were used to grow the oxide, based on the concept, found in the literature, that with very low current flow, the OH^- became the mobile species. The concept was that any elemental arsenic remaining in the oxide would be oxidized by passing OH^- ions. Finally, fluoride ions were forced into the oxide by field-aided diffusion, with the objective of reacting them with any excess arsenic in the oxide. Each of these treatments improved the electrical properties of the oxide.

Using these few treatments, all initiated in the last few months of the contract, we were able to lower the density of interface states

of the GaAs/oxide interface by at least a factor of ten. The improvement may have been better, but the Terman method of measurement was too insensitive to measure the density in some regions of the bandgap. And the quasi-static method (not usable with the high densities observed earlier and with the conducting oxide) was not applied because of lack of time.

Conclusions

The difficulty found with GaAs oxidation is expected to be common to III/V compounds, although possibly in not such a dramatic form. The difficulty, as mentioned above, is the tendency of one of the lattice ions of the compound to be much more easily oxidized than the other. This will lead to undesirable etching patterns and oxidation mechanisms unless the feature is recognized and studies are undertaken to learn how to adjust the chemistry.

We initiated such studies for the case of GaAs in this work, but have not had time to explore the problems in enough detail, or, actually enough time to evaluate sufficiently the success of the studies made. Thus, although substantial progress was made in understanding and correcting the problem, many further improvements are anticipated in this interdisciplinary area.

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Anodically grown oxides on GaAs were produced and their electrical properties measured by electrochemical techniques. It was concluded that residual unoxidized arsenic dissolved in the oxide causes poor insulating characteristics, and methods to correct the problem were examined.

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